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Modeling Optimization and Recovery of High-Purity Magnesium Oxide from Bittern Using Ammonia Precipitation.

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ABSTRACT

A central composite design (CCD) Model was used for fitting quadric model equations that helps in optimizing the effective selected parameters. The optimal Magnesium oxide yield was analyzed by XRF, XRD and FTIR. Magnesium oxide crystallization was observed by SEM / EDX analysis. Results revealed that most controlling parameter governing precipitation process was ammonia mass giving maximum yield of magnesium oxide crystals. A good achievement of modeling and optimization of chemical precipitation and clarifying the model validation was discussed.

Keywords: Magnesium oxide, Modeling, optimization, ammonia, Bittern

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INTRODUCTION

High purity 94.46% magnesium oxide (MgO) can be obtained by ammonia precipitation Method from sea water bittern. NH_4 Cl can be used effectively for precipitation reaction as raw material [1]. Recently magnesium oxide performed excellent chromatographic separation [2]. It is also used as packing material with excellent retention property for separation of aromatic hydrocarbon [3]. When magnesium oxide is prepared with high activity it is capable to be used in many applications. In chemical applications magnesium oxide can be used as a promoter and activator for halogen-free polymeric materials [4] and [5]. Magnesium oxide is used as support in the field of catalysis [6]. It can be employed for dehydrogenation – dehydration of alcohols, dehydrohalogenation of halogenated hydrocarbons [7] and it can be used in synthesis of pyranopyrazole derivatives [8]. Also the natural dolomite, (Calcium oxide and Magnesium oxide) rock as green catalyst has been used for biodiesel synthesis [9]. The objective of this work is the selection of experimental design methodology to maximize magnesium oxide yield by indicating optimum experimental conditions in least laboratory experiments.

MATERIALS AND METHODS:

Different magnesium ions concentration were prepared from natural purified concentrated bittern containing 80 g/L Mg^{++} ions. The magnesium ions concentration was determined by EDTA chelating titration method for all experiments.

Using NH_4OH solution as strong base with different molar ratio for precipitating magnesium hydroxide $Mg(OH)_2$ according to Indian patent(20100172812).

All precipitating experiments were performed at room temperature with different time of stirring (30 min-90 min) at pH=10. $Mg(OH)_2$ was obtained as white precipitate which was washed with distilled water and dried at 110 °C till constant weight.

All hydroxide powders were calcinated at needed temperatures (800°C - 1100 °C). All calcined yields were washed with distilled water and dried at 110 °C.

The optimum magnesium oxide agglomerate was examined using XRF, FTIR, and SEM /EDX analysis.

Five factors were chosen for investigating optimization of MgO from sea water bittern.

(X_1) magnesium ion concentration (45 g/L – 105 g/L).
(X_2)Stirring time for precipitation reaction completion using mechanical bad, (30 min – 90 min).
(X_3) Ammonia concentration (mass) (76 g/L – 172 g/L).
(X_4) yield of MgO (21.7 g/L – 117.58 g/L).
(X_5) Calcination temperature (800 °C – 1100 °C).

Response surface methodology:

It is a statistic empirical technique which depend mainly on the quantitative analysis of obtained data from appropriate designed experiments to determine regression model and operating conditions [10], [11], and[12]. In this study, the design was done using central composite design (CCD) where different five levels of selected independent variables in a wide range when compared with Box-Behnken Design and Face Centered design which are based on only three levels for variables. CCD method is convenient for fitting quadratic model equations for surface and help optimizing the effective parameters with a minimum number of experiments as well as analyzing the interaction between selected parameters. The full model equation with linear and quadratic terms for predicting the optimal response was given as independent variables and their coded levels for the central composite design in Table 1. Each run was an average of triple repetition [13]. A polynomial model, with p + 1 coefficient, is proposed to relate the experimental response to be optimized, y, with the k factors through the p variables (p ≥ k) as shown in Eq.1.

$$Yi = b0 + b1x1 + b2x2 + \ldots + bkxk + b11x12 + b22x22 + \ldots + bkkxk2 + b12x1x2 + \ldots + b1kx1xk + \ldots + bk\text{-}1,k\ xk\text{-}1xk\ x1 \quad (1)$$

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where x k+1,xk+2, …, xp are the cross-products and powers of the k factors, x1, x2…xk, are the codified factors.

RESULTS AND DISCUSSION

Table 1: Studied factors and experimental domains for central composite model

Effect	Factors	-2	-1	0	+1	+2	Increment
X1	Precipitation Reaction Time, (t, min)	30	45	60	75	90	15
X2	Calcination Temperature, (T, ºC)	800	900	1000	1100	1200	100
X3	Mg conc. [Mg g/l]	45	60	75	90	105	15
X4	Ammonia Solution mass, gm	76	100	124	148	172	24

These four selected factors with their domains were selected among many others controlling the precipitation of magnesium salts from bittern as reactions time, reaction temperature, and reactants stoichiometry and others controlling calcination process as calcination temperature, and calcination duration. This new mixed study was introduced in this work to know theeffect of different parameters on the whole process for production of magnesium oxide from bittern.

Table 2 : Central Composite model data used to model the precipitation of magnesium salts from bittern and its calcination to MgO yield and % Mg unreacted (remains) in bittern

No	X1	X2	X3	X4	X1 (time of reaction, min	X2 (Calcination temperature , ºC)	X3 (Mg conc.in bittern , g/l)	X4 (Mass of Ammonium hydroxide)	Y1 , Yield of MgO	Y2, % Magnesium remains
1	-1	-1	-1	-1	45	900	60	100	77.38	47.28
2	1	-1	-1	-1	75	900	60	100	73.74	49.46
3	-1	1	-1	-1	45	1100	60	100	72.88	45.80
4	1	1	-1	-1	75	1100	60	100	78.18	48.20
5	-1	-1	1	-1	45	900	90	100	77.12	48.09
6	1	-1	1	-1	75	900	90	100	114.755	38.23
7	-1	1	1	-1	45	1100	90	100	113.74	38.55
8	1	1	1	-1	75	1100	90	100	117.58	34.34
9	-1	-1	-1	1	45	900	60	148	21.71	63.23
10	1	-1	-1	1	75	900	60	148	13.52	65.34
11	-1	1	-1	1	45	1100	60	148	16.12	64.32
12	1	1	-1	1	75	1100	60	148	32.75	58.62
13	-1	-1	1	1	45	900	90	148	22.51	61.72
14	1	-1	1	1	75	900	90	148	33.52	57.93
15	-1	1	1	1	45	1100	90	148	28.53	59.53

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16	1	1	1	1	75	1100	90	148	27.98	59.43
17	-2	0	0	0	30	1000	75	124	119.42	37.53
18	2	0	0	0	90	1000	75	124	56.16	54.23
19	0	-2	0	0	60	800	75	124	55.26	56.32
20	0	2	0	0	60	1200	75	124	54.25	53.32
21	0	0	-2	0	60	1000	45	124	91.89	41.78
22	0	0	2	0	60	1000	105	124	88.63	39.73
23	0	0	0	-2	60	1000	75	76	88.82	36.72
24	0	0	0	2	60	1000	75	172	89.11	39.12
25	0	0	0	0	60	1000	75	124	93.11	40.22
26	0	0	0	0	60	1000	75	124	94.22	41.32

In Table 2, the experimental data for MgO yield (Y1) and %magnesium remains (Y2)analyzed out by running all 26 experiments were presented.

Table 3: Analysis of variance for yield of MgO precipitated from bittern using ammonia solution

@Nemrodw					
	df	***SS***	***MS***	***F_{95}***	***Signification***
Regression	14	16789.5	1199.25	2.71	1.78*
Residuals	11	12061.3	1096.48		
Validate	10	12060.6	1206.07		1.76*
Total	25	28850.7			

The analysis of variance(NEMROWD) for this study on Magnesium oxide yield (Y1) precipitated from bittern by means of ammonia and % Mg remaining in bittern(Y2) were used in order to ensure a valid model for optimizing selected variables. The results of the second-order response surface model fitting are given in Tables 3 and 4.The larger magnitude of the Fisher values (Upper 5% points -F_{95}) after being valid by means of significance, the more significance shown as the presence of number of asterisks as signification level.

Table 4 : Analysis of variance for 2nd model response as % magnesium unreacted remaining in bittern.

@Nemrodw					
	df	***SS***	***MS***	***F_{95}***	***Signification***
Regression	14	1487.15	106.225	2.71	35.8
Residuals	11	932.35	84.48		
Validate	10	931.74	93.17		6.3
Total	25	2419.5			

It was clear from Table (5) that the Composite Central model gives the effect of each variable on 1st and2nd response and the interaction between these variables based on quadratic functions coefficients. Based on data for yield of MgO crystals Y1, It was affected with the four variables but the most important one was the ammonia mass ($\mathbf{X_4}$) and the quadratic function of calcination temperature ($\mathbf{X_2^2}$) expressed as signification percent as shown in equation1.But for% unreacted magnesium remaining in bittern Y2,the variables X1, X2, and X3have no influence on it which was shown by signification percent of these parameter coefficients shown in Table (5). This can be attributed to the fact that the selected parameters were governing the whole process for precipitation and calcination for the precipitated magnesium salts, and so the effect of magnesium concentration remaining in bittern was governed only with X4 (ammonia mass) expressing the reaction stoichiometry as the most controlling parameter governing the precipitation process.

Table 5 : Variable coefficients using NEMROWD for experimental responses

Coefficient	Value	Standard deviation	t.exp	Signification%
Y1				
b1	-2.687	1.38	-16.77	3.79*

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b2	2.145	1.38	13.39	4.75*
b3	5.956	1.38	37.17	1.71*
b4	-22.006	1.38	-137.36	0.463**
b11	-5.272	1.48	-28.06	2.27*
b22	-13.530	1.48	-72.02	0.884**
b33	-4.654	1.48	-24.77	2.57*
b44	-4.978	1.48	-26.50	2.40*
b12	-0.725	1.18	-3.69	16.8
b13	2.615	1.18	13.33	4.77*
b14	1.647	1.18	8.39	7.6
b23	-1.515	2.21	-7.72	8.2
b24	-1.579	2.21	-8.05	7.9
b34	-5.786	2.21	-29.49	2.16*
Y2				
b0	40.765	1.48	6.26	< 0.01***
b1	0.684	1.48	0.36	72.3
b2	-1.188	1.48	-0.63	54.0
b3	-2.02	1.48	-1.08	30.5
b4	5.875	1.48	3.13	0.965**
b11	2.514	1.00	1.14	27.8
b22	4.7419	1.00	2.16	5.4
b33	1.233	1.00	0.56	58.7
b44	0.774	1.00	0.35	73.2
b12	0.111	1.00	0.05	96.3
b13	-1.186	1.00	-0.52	61.7
b14	0.124	1.00	0.05	95.8
b23	-0.361	1.00	-0.16	87.8
b24	0.614	1.00	0.27	79.3
b34	1.166	1.00	0.51	62.3

The obtained regression model equation for Y1 and Y2 with the selected significant variables and their interactions is as follows:

Y_1(MgO yield) = b_0 + (b_1X_1+ b_2X_2+ b_3X_3+b_4X_4)+($b_{13}X_1X_3$ + $b_{34}X_3X_4$)+($b_{11}X_1^2$ +$b_{22}X_2^2$+$b_{33}X_3^2$+ $b_{44}X_4^2$)

Y_1(MgO yield)= 0– 2.687 X_1+2.145X_2+ 5.959 X_3-**22.006X_4**+15.615 X_1X_2–12.22 X_1X_3-5.272 X_1^2– **13.53 X_2^2** – 4.654 X_3^2 – 4.978 X_4^2 .....(1)

Y_2(%Mg unreacted)= b_0 + (b_4X_4)

Y_2**(%Mg unreacted)**= 40.765+5.875 X_4.....(2)

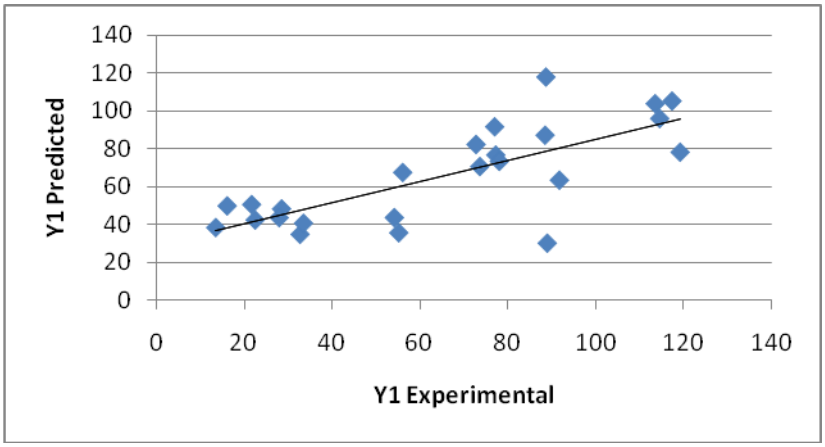

Fig (1): The relation between Experimental and predicted values for yield of MgO

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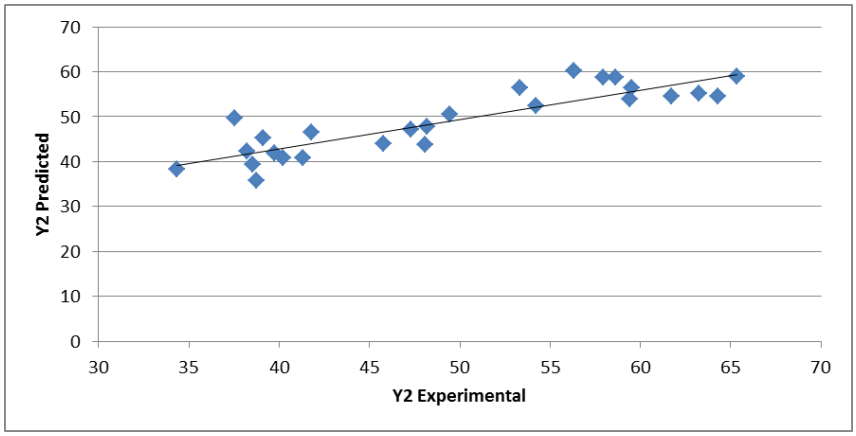
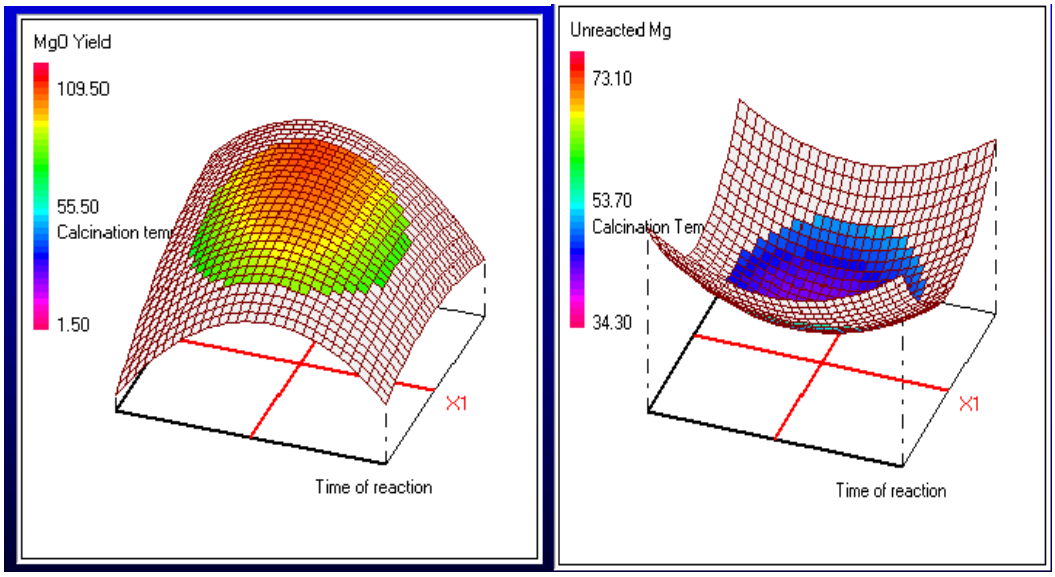


Fig (2): the relation between experimental and predicted values for unreacted Mg % in reaction mixture

It was concluded from figures 1 and 2 that the experimental and predicted values for the 1st and 2nd responses shows a the same trend to a certain extent and then an optimum was suggested by the validated model which suggested 75 min (reaction time) , 1075ºC calcination temperature, 86.72 g/l magnesium concentration with ammonia mass of 154.24 g giving a maximum yield of MgO crystals.

The effect of selected parameters and their interaction on yield of MgOwill be shown in figures from 3 to7 giving the 3D effect of two parameters on yield and % unreacted while keeping the other two variables on the center point.



Fig(3): Effect of time of reaction and calcination temperatures on MgO yield and unreacted magnesium ions

It was obvious from Fig(3) the influence of calcination temperature from 800-1200ºCand time of reaction from (30-90 min) on the yield of magnesium oxide and % unreacted of magnesium ion remaining in bittern to give a maximum of 109.5 g and a minumum of 34.3% when the time of reaction 60 min and calcination temperature of 1000ºC when X3 and X4 are taken at the center points.

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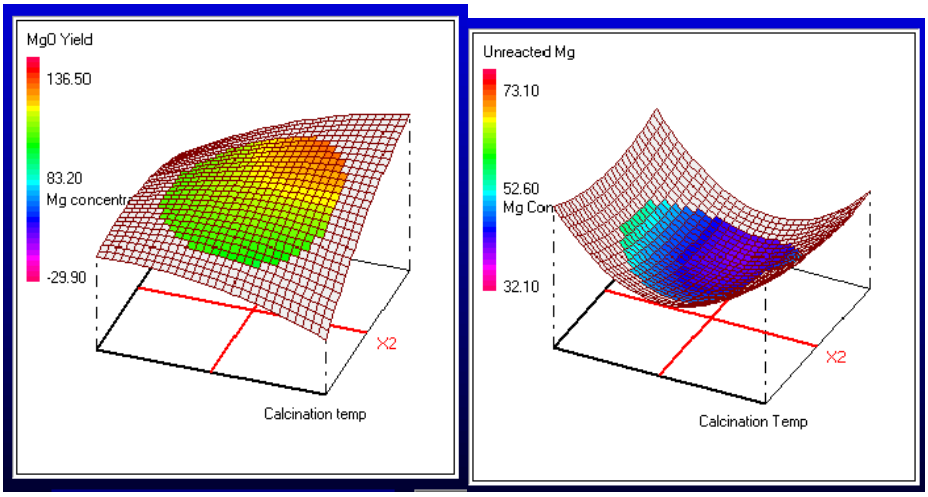

Fig (4): Effect of calcination temperature and magnesium concentration on MgO yield and unreacted magnesium ions

For a better desirability of variables and understanding the interaction between significant variables, three-dimensional 3D plots for the measured responses based on model equations (Eqs.1 and 2) between the calcination temperatures with the magnesium concentration were shown in Fig (4). It indicates the clear enhancement of calcination temperature on MgO yield that it increases 83.2 g at 1000ºC which was raised to reach 136.5 g with the increase in calcination temperature with magnesium concentration in bittern, on the contrast for unreacted magnesium remained in bittern which appears to be unaffected with the increase in temperature and shows a minimum of about 32 % at the middle level of calcination temperature and Mg concentration.

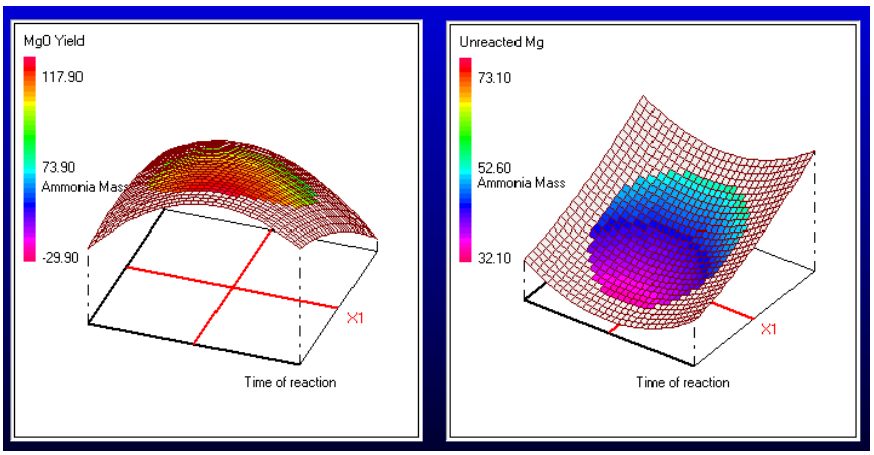

Fig (5): Effect of time of reaction and ammonia mass onMgO yield and unreacted magnesium ions

Also, the influence of ammonia mass seems to be the most important variable controlling this reaction for precipitation and calcination of magnesium salts from bittern and this will be illustrated and justified as well in Fig (5) and Fig (6).

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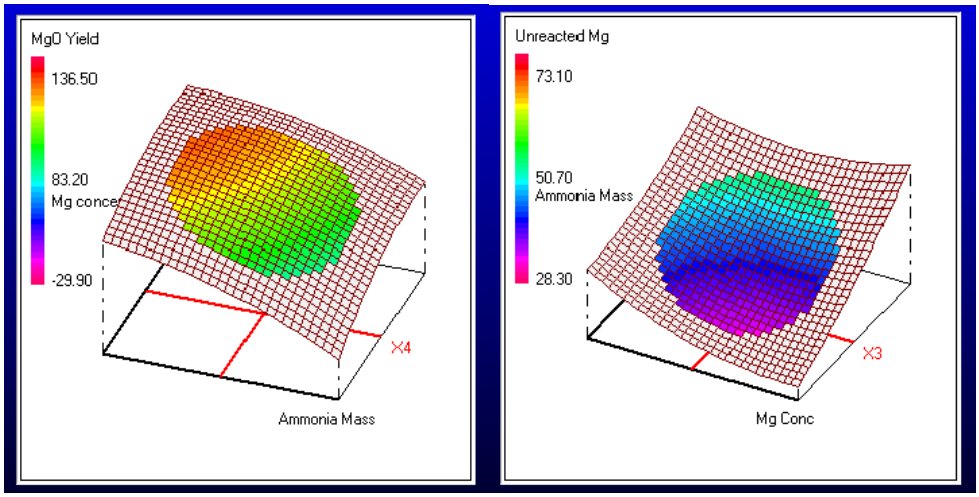


Fig (6): Effect of magnesium concentration and ammonia mass on MgO yield and unreacted magnesium ions

The maximum level for magnesium oxide yield was only 117.9 g when the ammonia mass increase from 124 to 172 g with the increase in time of reaction which has an adverse effect on the overall process yield ; on the other hand one can notice the difference in figure 6 where the decrease in ammonia mass slight below the middle favored the yield of formed MgO to reach a maximum of 136.5 g with the middle value of magnesium concentration. The same for a minimum reached for %magnesium ions, which gives about 28%with the decrease in ammonia mass.

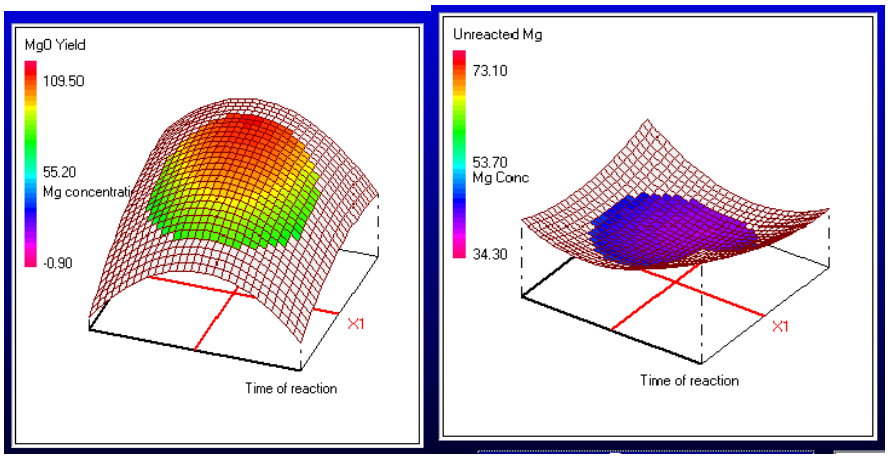


Fig (7): Effect of magnesium concentration and time of reaction on MgO yield and unreacted magnesium ions

It can be concluded from figure 7 that calcinated MgO yield was considerably influenced with the increase in starting magnesium concentration in bittern over progress of reaction with almost invariable unreacted magnesium percentage which can be attributed that the increase in magnesium concentration have no effect on reaction conversion with time of reaction in presence of ammonia mass which seems to be the controlling reactant on yield which decreases to be only 109.5 g with about 34% unreacted magnesium which means that magnesium was precipitated mainly as magnesium hydroxides which easily calcinated to form MgO at the studied calcination temperatures range with other forms which didn't converted to magnesium oxides. It can be concluded from Figures 3–7 that the optimum conditions were quite efficient to trap 136.5 g recovered magnesium oxide crystals calcinated and precipitated from bittern at 75 min (reaction time) , 1075ºC calcination temperature, 86.72 g/l magnesium concentration with ammonia mass of 154.24 g where all insignificance effect for variables were calculated near its value on the middle point. The dependence of magnesium precipitation from bittern and calcination using ammonia solution was very clear through validated model to be highly influenced by time of reaction, calcination temperature, concentration of

magnesium in bittern and mass of ammonia. The optimized parameters according to selected responses were automatically adjusted in the studied ranges using applied software for model validation.

Characterization and Analysis of Magnesium oxide:

X-ray fluorescence analysis XRF:

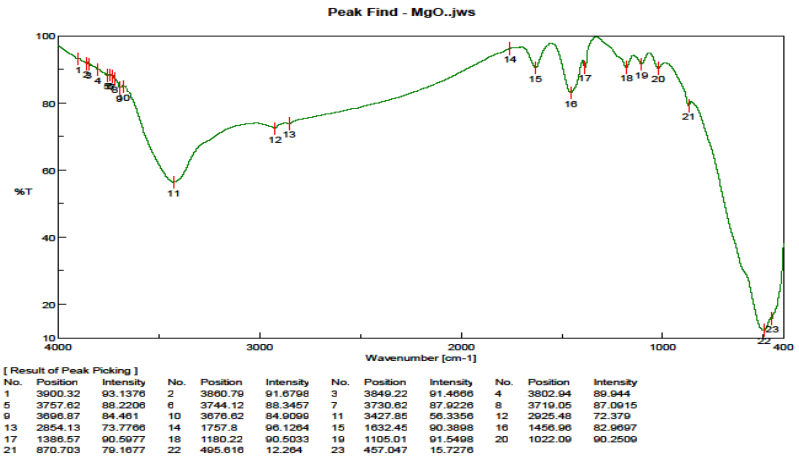
An instrumental Axios advanced , Sequential WB – Spectrometer, PANalytical 2005 model was used. Magnesium oxide was precipitated with calculated optimized conditions revealing the powder characterized in Table (6). The table shows MgO weight percent 94.46% with loss of ignition 1.86 weight percent.

Table(6): Elemental analysis of MgO using XRF:

Main Constituents in	(wt %)
SiO_2	0.94
Al_2O_3	0.28
Fe_2O_3	0.03
MgO	94.46
CaO	0.05
Na_2O	0.42
K_2O	0.11
P_2O_5	0.02
SO_3	0.77
F	0.27
Cl	0.46
LOI	1.86
MnO	0.006
NiO	0.005
CuO	0.006
ZnO	0.313
WO_3	0.007

Infrared spectrometry analysis (FTIR):

The instrumental Fourier transform infrared spectroscopy (FTIR) spectra of Magnesium oxide was measured in 4000-400 cm^{-1} wave number range. The functional groups corresponding to magnesium oxide were studied.



Fig(8): FTIR spectra of magnesium oxide at optimum calculated conditions.

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The spectra revealed several intense peaks indicating the presence of main functional groups as made magnesium oxide. Based on Fig(8) a broad band at 3427 cm^{-1} is corresponding to the stretching mode of hydroxyl groups due to physical adsorption of molecular water. While the peak appeared at 1632 cm^{-1} illustrates bending mode. The peak appeared at 2954 cm^{-1} presents C-H symmetric and anti-symmetric stretching vibration. The peak illustrated at 1456 cm^{-1} can be attributed to Mg-O stretching vibrations. The peak present at 1180 cm^{-1} is due to the H^+ ions and the peak illustrated at 870 cm^{-1} is correlated to Mg-O stretching vibration.

Scan Electron Microscope SEM:

The instrumental analysis was performed using (SEM) model Quanta 250 FEG (yield Emission Gun) attached with EDX Unit (Energy Dispersive &ray Analysis with accelerating voltage 30 K,V., modification 14X up to 100000 and resolution for Gun In).

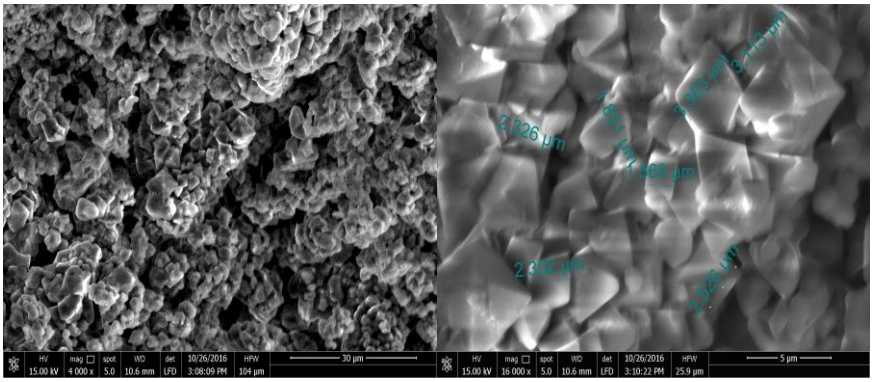

Fig (9_a) and Fig(9_b): showing SEM Pictures and morphology of MgO

Fig (9_a) and Fig (9_b) showing the hexagonal crystal structure into cubic structure indicating MgO occurance. The homogeneous distribution related to perclase phase and crystal size ranged from 2.3µm to 3.3 µm.

		Eleme	Weight %	Ato	Net	Error %			
		O K	40.	50.	27.	9.87			
		Mg	59.	49.	94.	6.4			

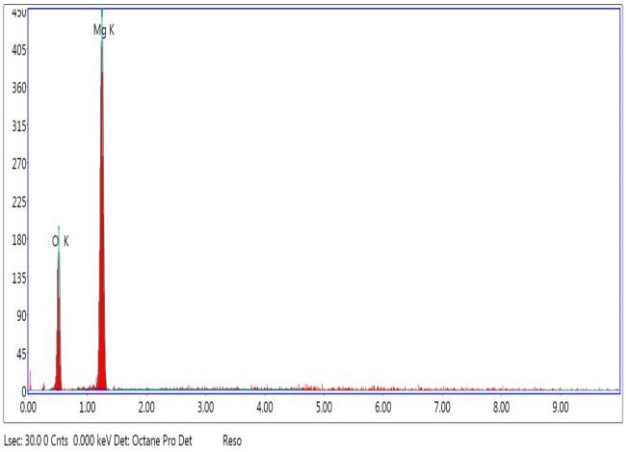

Fig (10): EDX analysis of MgO yield

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The elemental analysis of MgO precipitated is shown in Fig(10). Weight percent of oxygen(O) and magnesium(Mg) was 40.18% and 59.49% respectively as main elements in the product.

X- Ray Diffraction Analysis:

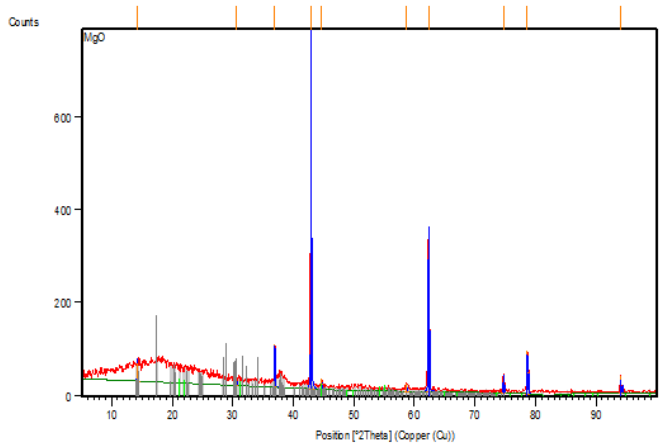

Fig (11): The XRD of optimized Magnesium oxide prepared

PA Analytical X-Ray Diffraction equipment mode X' pert PRO with Monochromatic Cu- radiation (ג = 1.5 uzA0) at 50 K.V., 40 M.A. and scanning speed 0.020/sec. were used. The reflection peak between 2Θ=20 and 600,corresponding spacing (d,A0) and relative intensities (I/I0) were obtained. The different charts and relative intensities are obtained and compared with ICDD files.

XRD charts represents high crystalline magnesium oxide calcined at 9000 °C.The yeild was improved by washing with water, the optimized MgO obtained after calcinations. Thus we achieved purity up to 94.46% as shown in the XRF results Table (6).

CONCLUSION

- A four factors central composite model design was employed in order to model and optimize the chosen responses (MgO yield, % Mg remains). According to the four factors fields, two valid models were established.
- It was clear that the maximum achieved yield for precipitated magnesium salts which was calcinated to give MgO salts from bittern was 136.5 g and a minimum unreacted magnesium of 28.2% at the optimized variables as given by the model which lie near the center point at most cases;75 min (reaction time), 1075ºC calcination temperature, 86.72 g/l magnesium concentration with ammonia mass of 154.24 g.
- This means that the selected 1st response was affected by the variables variation to a certain extent but for the second one; it is not. These results represent a good achievement of modeling and optimization of chemical precipitation and clarifying the influence of selected parameters and thus model validation with insignificance parameters.
- Finally, an easy, simple, and cost effective method for the pre-cipitation of valuable magnesium salts with the ease of formation of magnesium oxide crystals.
- Synthesis of Mg O with aqueous ammonia revealed the formation of hexagonal and cubic-shaped particles with different crystal size ranging from 2.3µm to 3.3 µm as shown by scan electron microscope morphology.
- The washed MgO reached 94.46% purity and confirmed by X-ray diffraction and XRF analysis. The calcination temperature for MgO ranges between 900 °C – 1100 °C. The product crystallinety was confirmed with the XRD and EDX analysis.

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